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Chemical equilibrium for the reactive system acetic acid + *n*-butanol + *n*-butyl acetate + water at 308.15 K

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ABSTRACT

Chemical equilibrium (CE) for the quaternary reactive system of acetic acid–*n*-butanol–*n*-butyl acetate–water was studied at 308.15 K and atmospheric pressure. The experimental data on CE were considered in comparison with the data on liquid–liquid equilibrium: the CE is reached both in homogeneous and heterogeneous area of reactive mixture compositions. The crossing of CE and binodal surfaces is presented in a composition tetrahedron and a square of transformed composition variables. The thermodynamic constant of CE at 308.15 K was determined with the use of NRTL and UNIQUAC models.

1. Introduction

The system with *n*-butyl acetate synthesis reaction is one of the most investigated systems. Due to a low environment impact *n*-butyl acetate is considered as convenient chemical solvent. It is also used in various industrial fields. The design of *n*-butyl acetate production demands special knowledge on phase and chemical equilibria (CE). Unfortunately, most researches have focused on the solubility and phase equilibrium (liquid–vapor and liquid–liquid). A short description of the investigations of phase equilibria in this system is presented in review papers [1,2].

The recent study on CE was carried out by Grob and Hasse [3] at 353.15–393.15 K. The data on CE in acetic acid–*n*-butanol–*n*-butyl acetate–water system at 358 K were obtained by Zhuchkov et al. [4] for 18 compositions. The data sets for CE at 101.3 kPa and boiling temperatures are presented in the paper of Lladosa et al. [5]. In papers [6,7] of Campanella and Mandagaran the coupled CE and phase equilibrium were considered.

The aim of our work is the study and the correlation of CE in acetic acid–*n*-butanol–*n*-butyl acetate–water system at 308.15 K and atmospheric pressure in wide composition region including homogeneous and heterogeneous areas of reactive solutions.

2. Experimental

2.1. Materials

n-Butanol (>0.99 mole fraction, Vekton, Russia) and *n*-butyl acetate (>0.99 mole fraction, Vekton, Russia) were purified by distillation, water was bidistilled. Acetic acid (>0.99 mole fraction, Vekton, Russia) was additionally purified by distillation, with the presence of 98% sulphuric acid. Purity was controlled by gas chromatography (GC) analysis (Table 1). The physical–chemical properties of pure substances are in a good agreement with the NIST data [8].

2.2. CE determination

The study of CE was carried out using GC analysis. Initial binary and ternary mixtures of known overall compositions were prepared in glass vessels (5 ml) by gravimetric method using an analytical balance Shinko VIBRA HT-120CE (Japan) with an accuracy of 0.001 g. Hydrochloric acid was used as a catalyst in amount of 0.003 mole fraction. Stirred up sealed vessels were placed in the liquid thermostat (308.15 K). The temperature uncertainty was ±0.05 K. The compositions of reacting mixtures were determined by GC analysis: the constancy of composition confirmed the reaching of CE. The CE was reached within few days (not more than 5 days). In case of splitting reactive mixtures the samples for the analysis were taken separately from water and organic phases. The chromatographic syringe (“Hamilton”, USA, 10 μl) was preliminary heated to avoid the splitting of samples. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal

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Table 1
The purities of the chemicals.

Substance	Purity, mole fraction[a]
Acetic acid	0.998
n-Butanol	0.995
n-Butyl acetate	0.998
Water	0.999

[a] The uncertainty is estimated to be ±0.002 mole fraction.

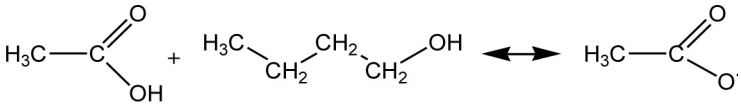
conductivity detector (TCD) and packed column Porapak R (1 m × 3 mm i.d.) was used. The TCD was chosen because of the presence of water. The carrier gas was helium with the flow rate of 60 ml/min. Operating temperatures of column, vaporizing injector and TCD temperature were 483 K, 503 K and 513 K respectively. The method of internal standard and relative calibration were used to determine CE compositions. Acetic acid was accepted as a linking component. Average uncertainty of GC analysis was ±0.005 mole fraction.

3. Results and discussions

3.1. Experimental data

The data on CE of acetic acid (1)–*n*-butanol (2)–*n*-butyl acetate (3)–water (4) system at 308.15 K and atmospheric pressure are presented in Table 2 (a heterogeneous region) and Table 3 (a homogeneous region).

In the case of ester synthesis reaction



the CE equilibrium compositions belong to the surface in composition tetrahedron.

According to the reaction equation, four binary subsystems (acetic acid–*n*-butyl acetate, acetic acid–water, *n*-butanol–*n*-butyl acetate, *n*-butanol–water) are nonreactive and should be considered as parts and borders of the surface of CE. Two binary systems (acetic acid–*n*-butanol and *n*-butyl acetate–water) and all four ternary subsystems are in chemically nonequilibrium states and do not belong to this surface. The surface of CE of the quaternary system acetic acid–*n*-butanol–*n*-butyl acetate–water at 308.15 K is presented in Fig. 1.

Fig. 1 also shows tie-lines that correspond to liquid–liquid envelope in a quaternary mixture with chemical equilibrium. Such tie-lines belonging to the curves of CE in ternary systems were called by Ung and Doherty as unique reactive tie-lines [9]. In the case of quaternary system linear surface formed by set of unique reactive tie-lines should be considered [10].

Table 2
The experimental data on CE for the quaternary system acetic acid (1)–*n*-butanol (2)–*n*-butyl acetate (3)–water (4) in the area of limited solubility (mole fractions *x*, 308.15 K, atmospheric pressure).[a]

Water phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.092	0.006	0.002	0.177	0.108	0.301
0.040	0.008	0.001	0.061	0.241	0.293
0.057	0.007	0.001	0.113	0.171	0.314
0.019	0.014	0.002	0.054	0.317	0.219
0.011	0.017	0.003	0.016	0.345	0.135
0.132	0.010	0.014	0.231	0.045	0.120

[a] Standard uncertainties $u(x) = 0.005$, $u(T) = 0.05$.

Table 3
The experimental data on CE for the quaternary system acetic acid (1)–*n*-butanol (2)–*n*-butyl acetate (3)–water (4) in the homogeneous region of composition (mole fractions *x*, 308.15 K, atmospheric pressure).[a]

x_1	x_2	x_3	x_1	x_2	x_3
0.469	0.025	0.230	0.142	0.126	0.465
0.310	0.066	0.295	0.060	0.262	0.473
0.154	0.160	0.319	0.357	0.030	0.501
0.068	0.300	0.299	0.212	0.071	0.511
0.029	0.444	0.247	0.088	0.173	0.528
0.560	0.016	0.238	0.024	0.337	0.538
0.400	0.038	0.298	0.283	0.038	0.587
0.231	0.106	0.375	0.144	0.101	0.611
0.112	0.221	0.358	0.037	0.248	0.623
0.046	0.373	0.320	0.165	0.065	0.686
0.019	0.540	0.260	0.062	0.157	0.709
0.485	0.025	0.312	0.090	0.081	0.772
0.309	0.065	0.383	0.536	0.015	0.147
0.161	0.151	0.406	0.374	0.039	0.209
0.071	0.294	0.392	0.035	0.376	0.213
0.377	0.039	0.402	0.466	0.021	0.144
0.209	0.095	0.423	0.297	0.062	0.208
0.103	0.197	0.418	0.014	0.455	0.146
0.276	0.057	0.464	0.374	0.028	0.131

[a] Standard uncertainties $u(x) = 0.005$, $u(T) = 0.05$.

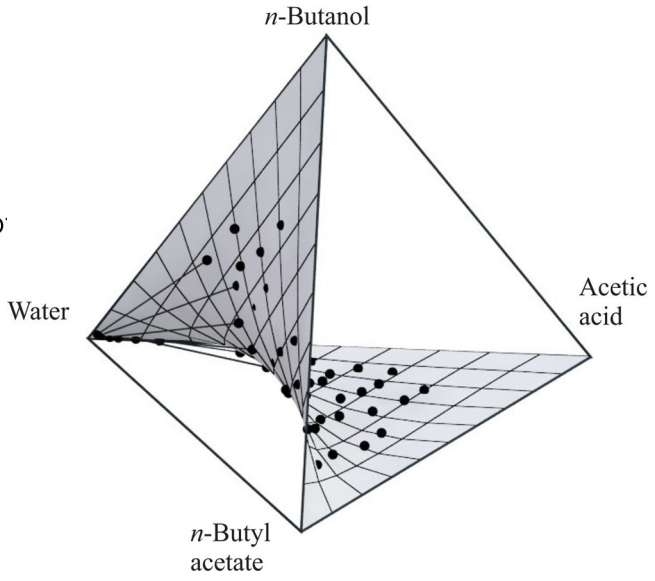


Fig. 1. The diagram of CE surface in acetic acid–*n*-butanol–*n*-butyl acetate–water system at 308.15 K. Black circles ●—experimental compositions corresponding to CE in homogeneous and heterogeneous area, straight lines—liquid–liquid tie-lines on the surface of CE.

The set of experimental results on CE and the disposition of liquid–liquid envelope at CE surface can also be presented using transformed composition variables, α_i (Fig. 2) [11,12].

In the case of considered reaction these variables are:

$$\alpha_1 = x_1 + x_4$$

$$\alpha_2 = x_2 + x_4$$

$$\alpha_3 = x_3 - x_4$$

where x_i is a molar fraction of specie *i*. As a result the composition space is a square of α-variables (Fig. 2). Such diagram gives a clear presentation of a disposition of liquid–liquid envelope at the surface of CE and the tie-lines that form a linear surface corresponding to CE in heterogeneous area. The binodal curve

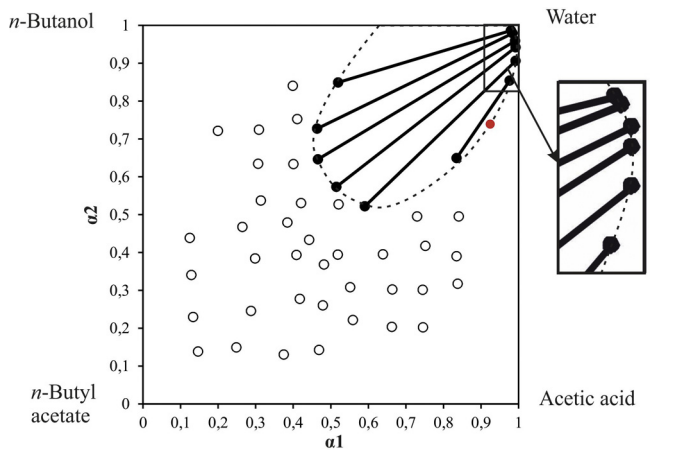


Fig. 2. The area of immiscibility at the surface of CE in acetic acid–*n*-butanol–*n*-butyl acetate–water system at 308.15 K: ●-●—liquid–liquid tie-lines, dash line—the binodal curve at CE surface, ○—composition points corresponding to CE in the homogeneous area (experimental results), ●—critical point of liquid–liquid equilibrium on the surface of CE.

on CE surface lies very close to "acid–water" side of composition square (or the edge of composition tetrahedron) but does not touch this side. The end points of binodal belong to "*n*-butanol–water" side i.e., to tie-line in this binary system.

Recently [13] we published the set of data on liquid–liquid equilibrium in acetic acid–*n*-butanol–*n*-butyl acetate–water system at 308.15 K for entire range of quaternary composition including ternary systems and chemically nonequilibrium states. The mutual disposition of CE and binodal surface is presented in Fig 3 which also demonstrates the intersection of these surfaces in the composition tetrahedron. Such intersection is in a good agreement with the results of present work.

4. Calculation of thermodynamic constant of CE

The analysis of the experimental data on CE was carried out with NRTL and UNIQUAC models. These models were used for calculations of activity coefficients. The thermodynamic constant of CE is related to the Gibbs energy of reaction by equation

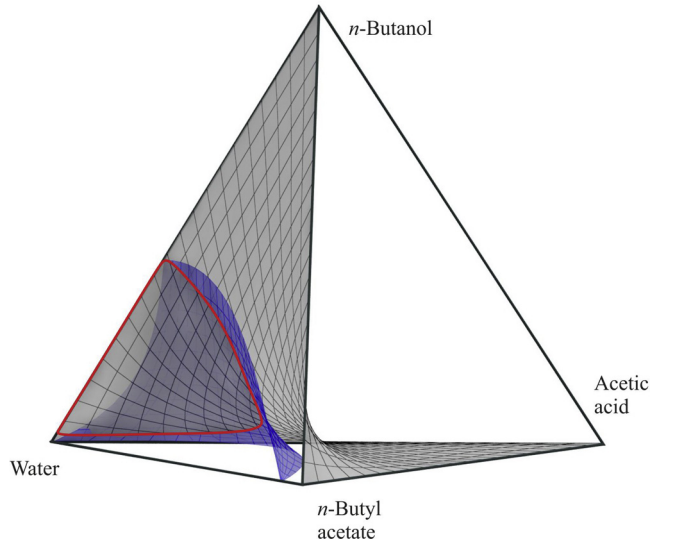


Fig. 3. The intersection of CE and binodal surfaces in composition tetrahedron. Gray color—CE surface, blue color—the binodal surface, red curve—the line of intersection of these surfaces. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$-RT\ln K_a = \sum_{i=1}^{n} \upsilon_i G_i^{\circ} = \Delta G^{\circ}, \tag{1}$$

where G_i°—Gibbs energies of pure components formation. The K_a could be also expressed in terms of activities of species. Accordingly the thermodynamic constant of CE was determined from our experimental data and calculated values of activity:

$$K_a = \Pi \alpha_i^{\upsilon_i}, \tag{2}$$

where α_i—activity, υ_i—stoichiometric coefficients of reactants and products that are negative and positive, respectively. The errors in such determination of K_a from experimental data are strongly dependent on the concentration. For example the concentration of species for some compositions is of the same order as an experimental error (~0.005). It can lead to a significant inaccuracy of K_a determination. Therefore K_a values were mostly calculated from the data for an average area of the chemical equilibrium surface where concentrations of all species are large enough.

4.1. NRTL model

Binary parameters for NRTL model were taken from paper [3]. We used NRTL equation for the activity coefficients γ_i in the solution of n components in the following forms [14]:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{i=1}^{m} x_i G_{ji}} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{i=1}^{m} x_i G_{ij}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{i=1}^{m} x_i G_{ij}} \right), \tag{3}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}, G_{ji} = \exp(-\alpha_{ji}\tau_{ji}), (\alpha_{ji} = \alpha_{ij}), \tag{4}$$

where g_{ji} is energy parameter characterized interaction of components j and i; parameter α_{ji} is responsible for the nonrandomness in the systems. The obtained constant of CE has a value 21.7 ± 2.3. This value of K_a includes only the experimental uncertainties, which are presented as a confidence interval with significant point of 0.05.

4.2. UNIQUAC model

Binary parameters for UNIQUAC model were taken from paper [15]. We used the equations for the calculation of activity coefficients in the following forms [16]:

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}), \tag{5}$$

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_{i=1}^{m} x_i \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} \sum_{i=1}^{m} q_i x_i \ln \frac{\Theta_i}{\Phi_i^*}, \tag{6}$$

$$\frac{g^E(\text{residual})}{RT} = -\sum_{i=1}^{m} q_i x_i \ln \left(\sum_{j=1}^{m} \Theta_j \tau_{ji} \right), \tag{7}$$

$$\Phi_*^i = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j}, \Theta_i = \frac{q_i x_i}{\sum_{j-1}^{m} q_j x_j}, \Theta_i' = \frac{q_i' x_i}{\sum_{j-1}^{m} q_i' x_j}, \tag{8}$$

$$\ln(\gamma_i) = \ln \frac{\Phi_*^i}{x_i} + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_*^i} + l_i - \frac{\Phi_*^i}{x_i} \sum_{j=1}^{m} x_j l_j - q_i' \ln \left(\sum_{j=1}^{m} \Theta_j' \tau_{ji} \right) + q_i' - q_i' \sum_{j=1}^{m} \frac{\Theta_j' \tau_{ij}}{\sum_{k=1}^{m} \Theta_k' \tau_{kj}}, \tag{9}$$

$$l_i = \frac{z}{2}\left(r_j - q_j\right) - (r_j - 1), \quad (10)$$

where r_i and q_i are the measures of molecular van der Waals volumes and molecular surface areas, respectively. The value of obtained constant of CE is 22.5 ± 1.7.

Values of constants of CE that were calculated by two models on the basis of our experimental data are in good agreement. The minor differences in these values could be explained by distinctions of the models. The average value of K_a is 22.1.

The obtained value of K_a is approximately the same as data presented in the paper [4] for 358.15 K where the constant of CE has value of 24. There are other results on K_a which also related to different temperatures. As an example, K_a at temperatures from 373.15 to 393.15 K was determined in [17] ($11.3 \leq K_a \leq 15.1$). In the work [3] the temperature dependences of K_a was proposed with the use of four different models at 353.15–393.15 K. The calculation of K_a at 308.15 K on the base of four equations [3] gives the values which have a strong distinction from each other. Probably the dependences from the work [3], which are related to the higher temperatures (353.15–393.15 K), could not be properly applied for $T = 308.15$ K.

The temperature dependence of K_a was also discussed in Refs. [18] and [19]. The results of calculation at 308.15 K with the dependences [18,19] give two values of K_a that are strongly differing from one another: 30.6 and 15.5 respectively. Unfortunately a lack of the data from papers [18] and [19] do not allow to determine what value is preferable. The value of our study $K_a = 22.1$ is approximately a cross between these quantities, $30.6 > K_a > 15.5$.

5. Conclusions

The chemical equilibrium in the quaternary reactive system acetic acid–*n*-butanol–*n*-butyl acetate–water at 308.15 K and atmospheric pressure was studied. The set of the new experimental data enables to present the chemical equilibrium surface in a composition tetrahedron. The CE is achieved in the homogeneous area and the heterogeneous area of reactive mixtures. Using NRTL and UNIQUAC models and experimental data the value of thermodynamic constant of chemical equilibrium at 308.15 was determined, $K_a = 22.1$.

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